SEMINAIRE ISMO

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Towards the full quantum simulation of complex systems. The problem of the representation of the interaction potential.

Quantum phenomena are ubiquitous and cannot be neglected if a physically correct molecular simulation is aimed for. Interestingly, despite the current boost in the development of dynamical methods, semiclassical or fully quantal, the availability and representation of Potential Energy Surfaces (PES) is still a major bottleneck, in particular for intermolecular interactions. In the case of grid-based quantum dynamical methods, the PES is represented globally, formally as a multidimensional tensor, whereas when considering on-the-fly approaches, the PES is expressed in a local representation at every time-step. In the first case, the limitation lies on the possibility of fitting the PES to an appropriate functional form for large number of degrees of freedom. Powerful and accurate as the existing methods are, a high degree of expertise is still required to master and apply these techniques, particularly when considering medium-large systems (>=6D), thus preventing their wider-spread use. In the second case, the limiting factor is the number of electronic structure calls (energies, gradients, Hessians, properties, etc.) needed to perform the propagation. Consequently, on-the-fly approaches are constrained to modest levels of theory.

In this talk, we present our novel approach to such problem: the Specific Reaction Parameter Multigrid POTFIT (SRP-MGPF) method, which provides a balanced solution to the aforementioned issues. SRP-MGPF allows in a single fitting process the generation of a potentially chemically-accurate (< 1 kcal/mol) global (molecular or intermolecular) PES at the cost of a semiempirical potential. The SRP-MGPF algorithm relies on three steps: (i) a fully automated topographical characterisation of a (inter)molecular PES in terms of minima, transition states, and minimum energy paths ; (ii) a global reparametrization of a semiempirical Hamiltonian (SRP) using reference geometries derived from the set of stationary points; and (iii) direct tensor-decomposition of the SRP PES into sum-of-products form with the MGPF algorithm. The SRP PES obtained at stage (ii) can be directly interfaced to any on-the-fly method and the SRP-MGPF PES, from stage (iii), is specifically designed to work the Multiconfiguration Time-Dependent Hartree (MCTDH) method. Illustrative examples of all these algorithms will be presented and as preliminary results for SRP-MGPF we shall compare MCTDH vibrational eigenstate calculations on a SRP-MGPF PES with previous highly accurate results for the benchmark HONO (6D) system. Finally, we shall discuss the interface of SRP PES with the Direct-Dynamics Variational Multiconfigurational Gaussian (DD-vMCG) method as well as with the Second Quantization extension of the Multilayer MCTDH (ML-MCTDH-SQR) algorithm.

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